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1 June 1999

FROM: PROI (TI) (STINFO)

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Fajardo, "Cryosolid Propellants - The Last "Revolutionary" HEDM Concept"

Presentation HEDM CONFERENCE

# **Cryosolid Propellants**

## **The Last “Revolutionary”**

### **HEDM Concept**

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## **Introduction**

“Revolutionary” vs. “Evolutionary” HEDMs  
HEDM Cryosolid Propellants

## **AFRL/Edwards Experimental Effort**

- + HEDM Dopant Source Development
- + Dopant Source Characterization
- + Cryosolids Characterization  
(thick, concentrated samples)

## **Summary**

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# “Revolutionary” vs. “Evolutionary” HEDM

“Revolutionary” means better than LOX/LH<sub>2</sub>

LOX/LH<sub>2</sub>                     $\Delta H_{sp} = 12.6 \text{ MJ/kg}$  (3.0 kcal/g)

HEDM Target:             $\Delta H_{sp} > 15.0 \text{ MJ/kg}$  (3.6 kcal/g)

Early (c1990) Revolutionary HEDM Concepts:

tetrahydrogen (H<sub>4</sub>)

metastable triplet helium (He\* and He<sub>2</sub>\*)

spin-polarized atomic hydrogen (H↑)

high-spin species (<sup>5</sup>CO)

dications (AB<sup>++</sup>, ABC<sup>++</sup>)

“non-metallics” (e.g., O<sub>4</sub>/H<sub>2</sub>, N<sub>4</sub>, N<sub>8</sub>, N<sub>20</sub>)

metallic hydrogen

metal atoms and clusters in solid H<sub>2</sub>

# HEDM Cryosolid Propellants Objectives

- \* Trap 5% molar concentration of energetic additives in solid hydrogen.
- \* Demonstrate size-scalable sample production method.

Grant V

# HEDM Cryosolid Propellants Payoffs

## Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$\begin{aligned} \text{LOX/LH}_2 : I_{sp} &= 390 \text{ s} \\ 5\% \text{ B/sH}_2 + \text{LOX} : I_{sp} &= 500 \text{ s} (+30\%)^* \end{aligned}$$

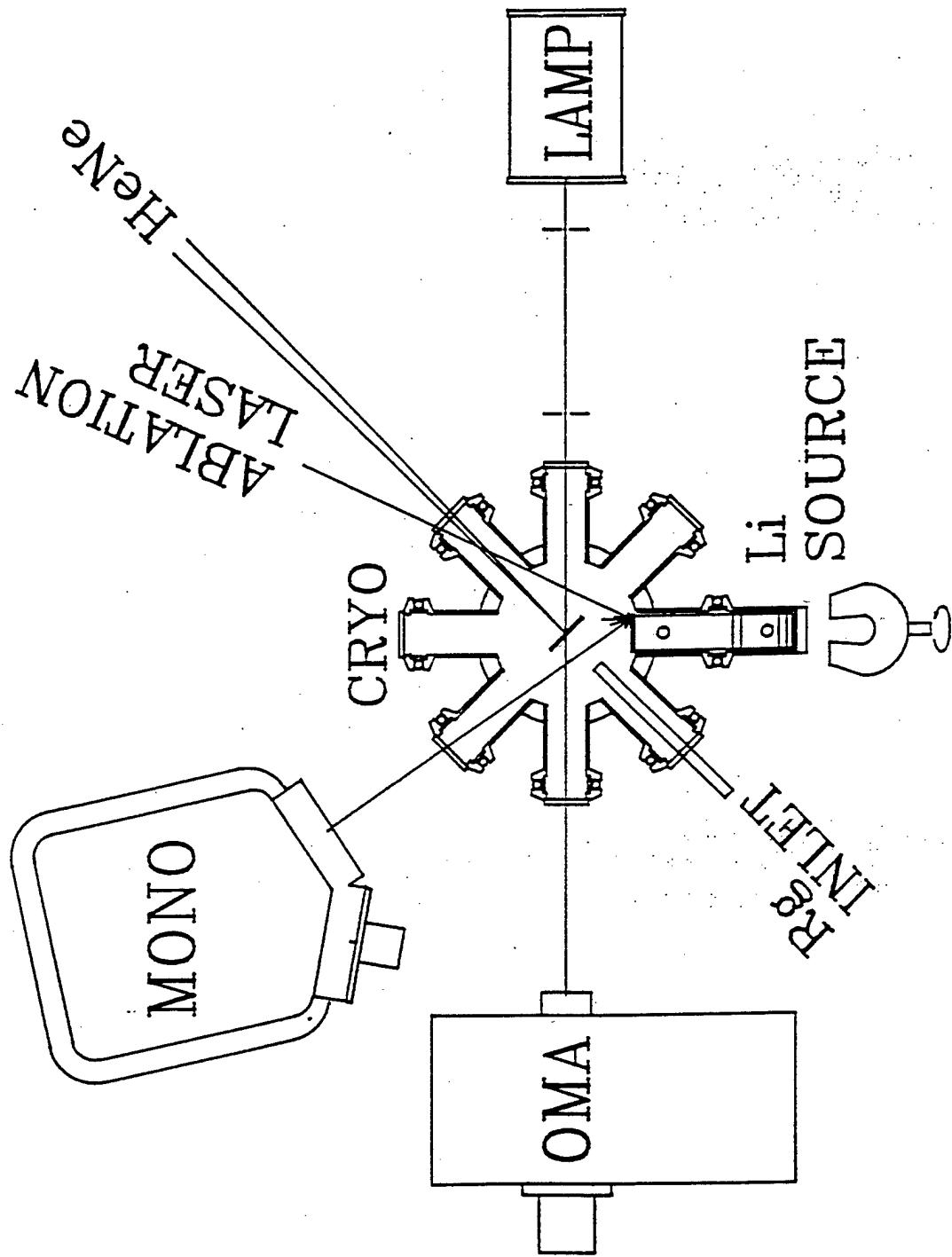
$\xrightarrow{350 \rightarrow 650}$

\* calculated for  $P_{\text{chamber}} = 1000 \text{ Pa}$ ,  $P_{\text{exhaust}} = 14.7 \text{ psia}$

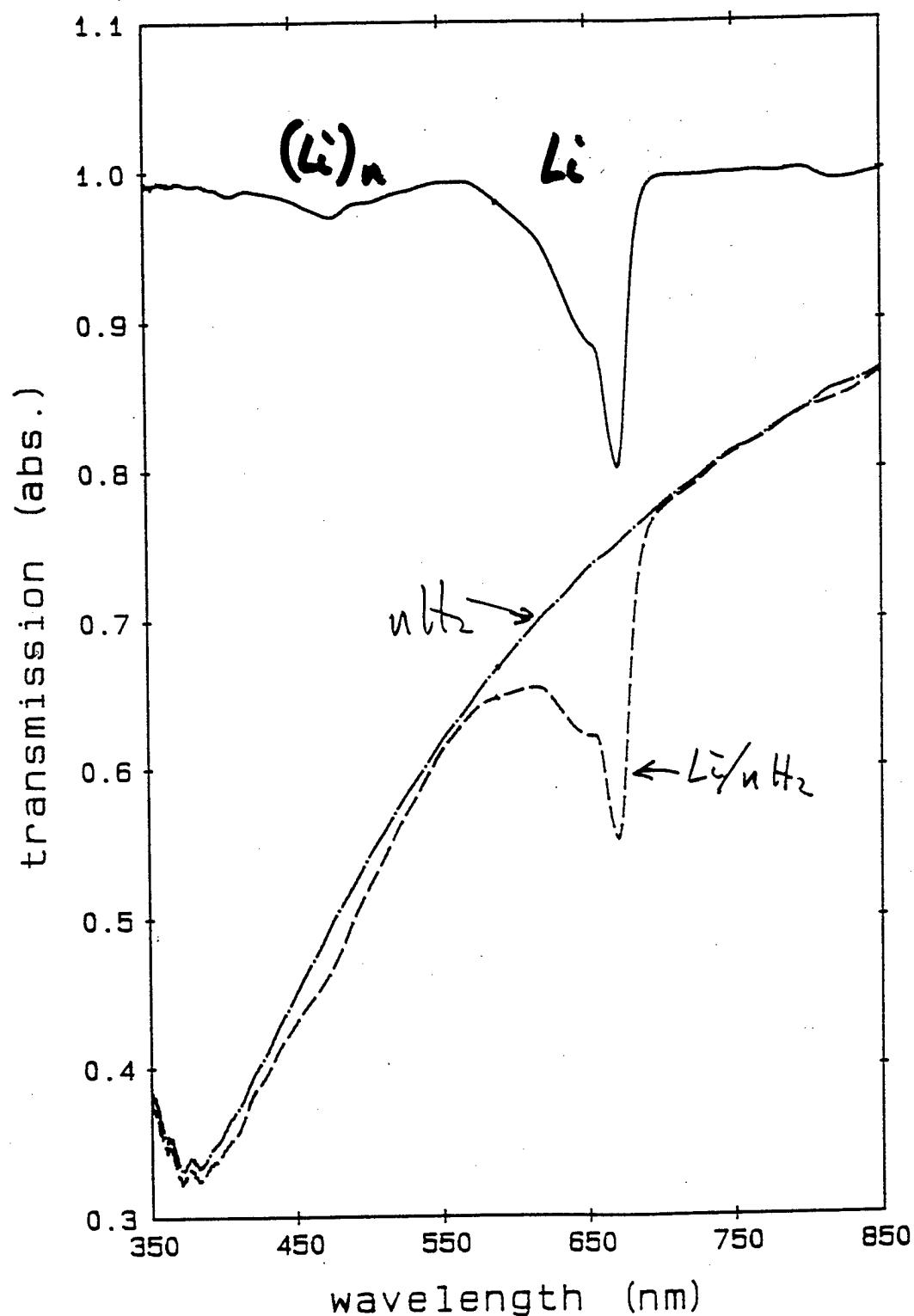
## Greater Propellant Density

liquid H<sub>2</sub> @ 20 K :  $\rho = 0.070 \text{ g/cm}^3$   
solid H<sub>2</sub> @ 2 K :  $\rho = 0.087 \text{ g/cm}^3 (+25\%)$   
50/50 liquid He/solid H<sub>2</sub> :  $\rho = 0.105 \text{ g/cm}^3 (+50\%)$

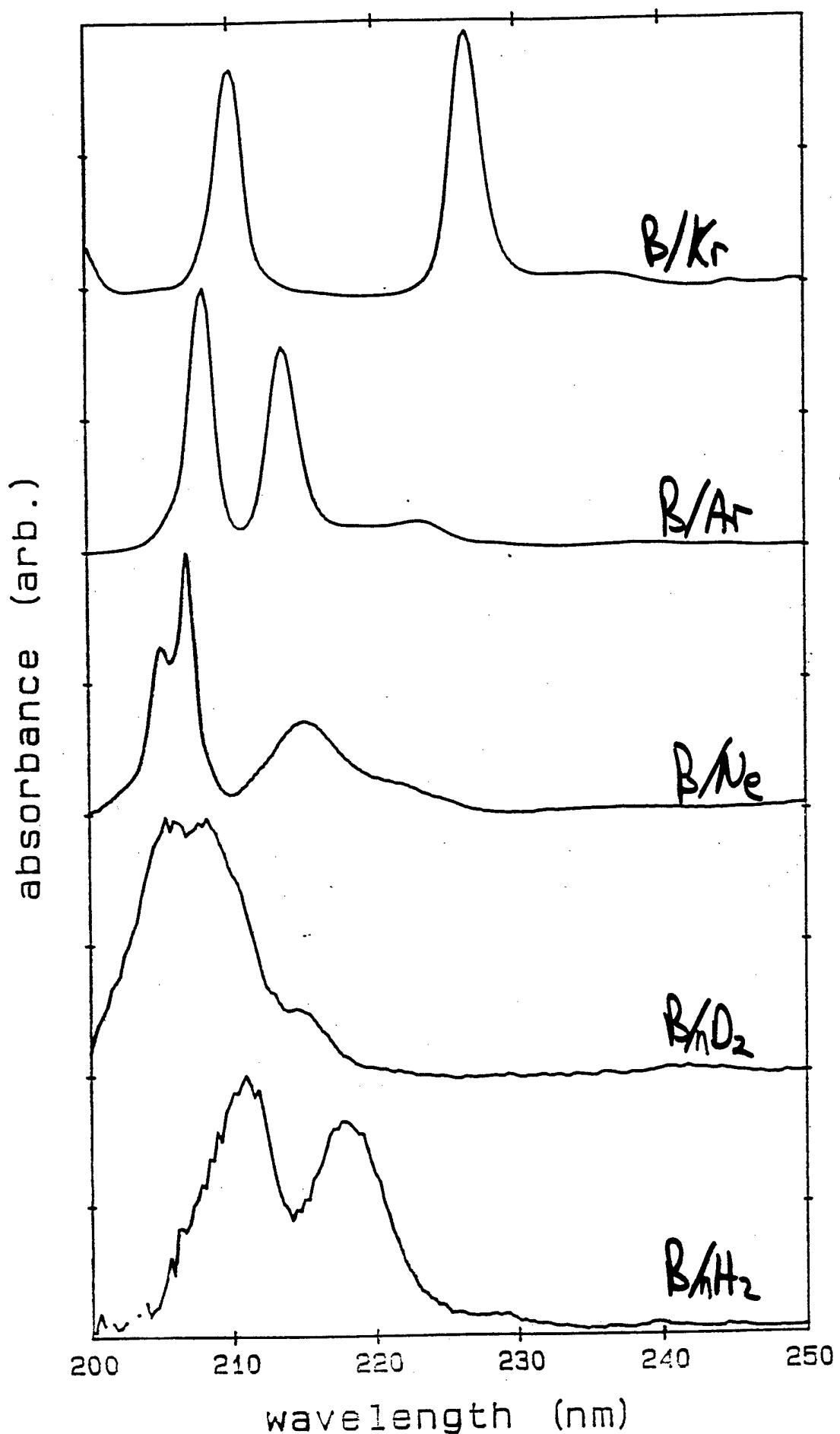
# Experimental Diagram (c.1993)



$\text{Li}/\text{H}_2$   $T=3\text{K}$

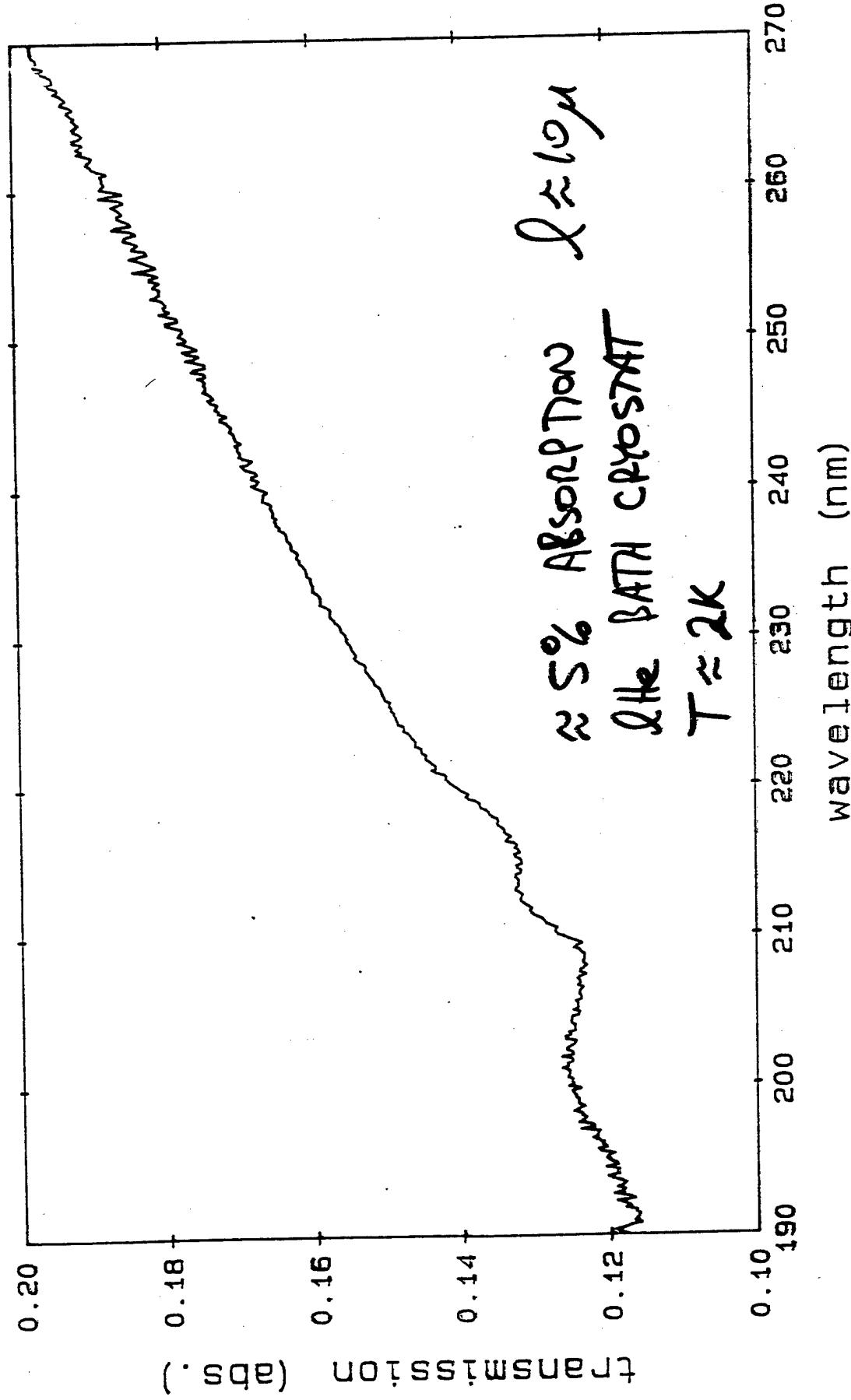


M.P. RAJARAO, J. Chem. Phys. 98, 110 (1993).



S. Tam + M. E. Fajardo, unpublished.

B<sub>6</sub>H<sub>2</sub> raw data (c1993)



# Optical Scattering in Solid Hydrogen

## Crystal Growing and Quality (p. 81)

“There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow.”

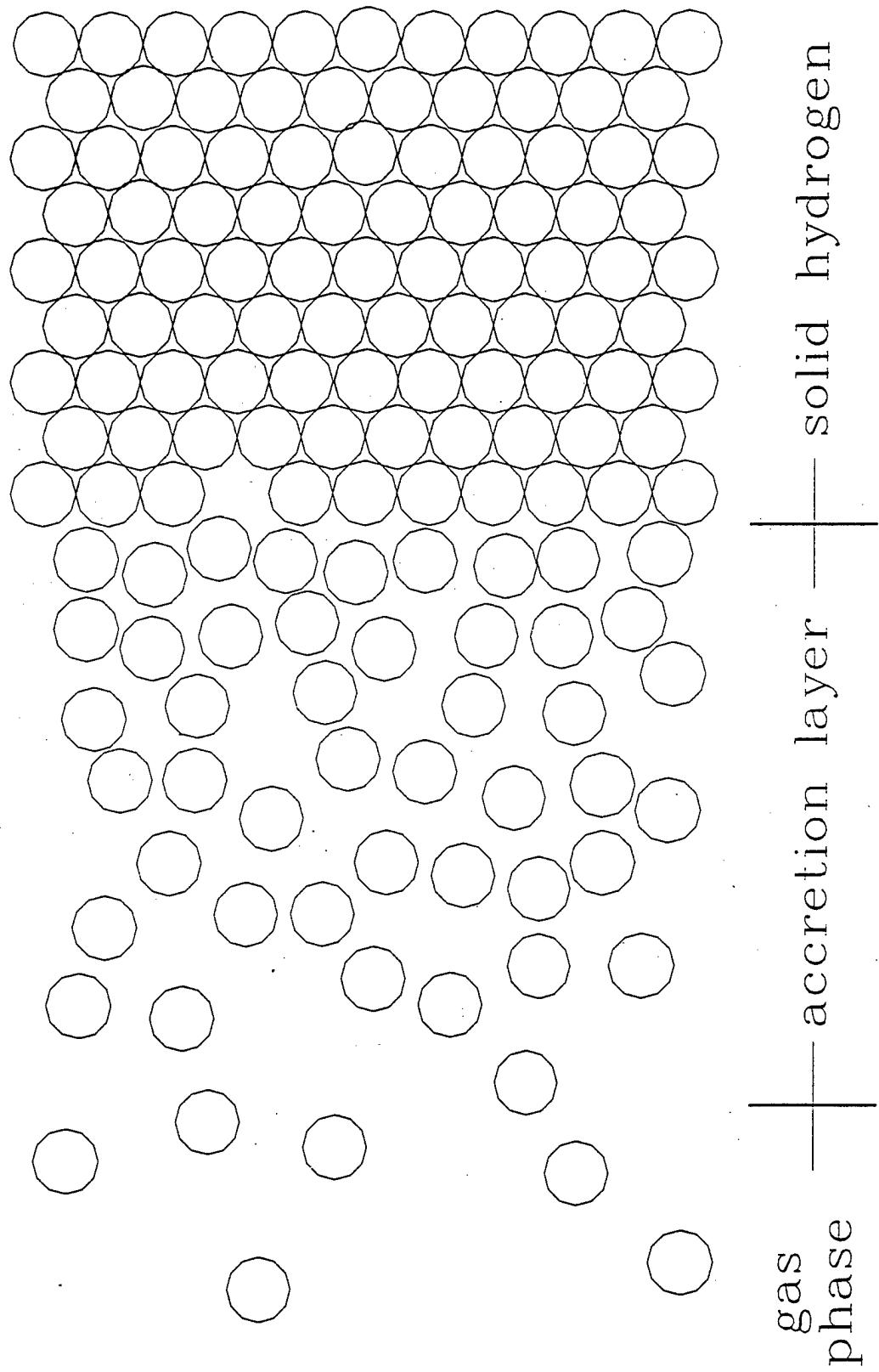
## Crystallite Light Scattering (p. 83)

“The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

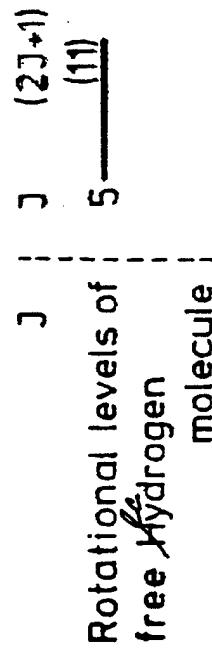
Yet a 1mm-thick layer of hydrogen crystallites can be a completely opaque brown-black.”

P.C. Souers,  
Hydrogen Properties for Fusion Energy  
(UC Press, Berkeley, 1986).

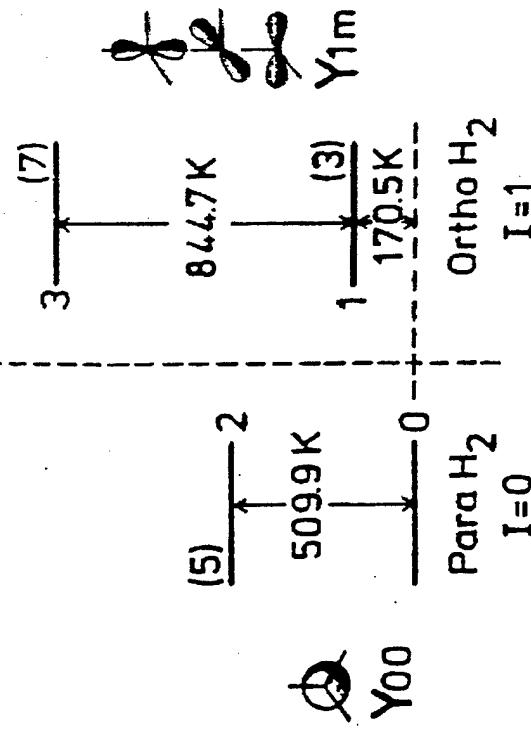
# Deposition Cartoon



# Ortho and Para Hydrogen



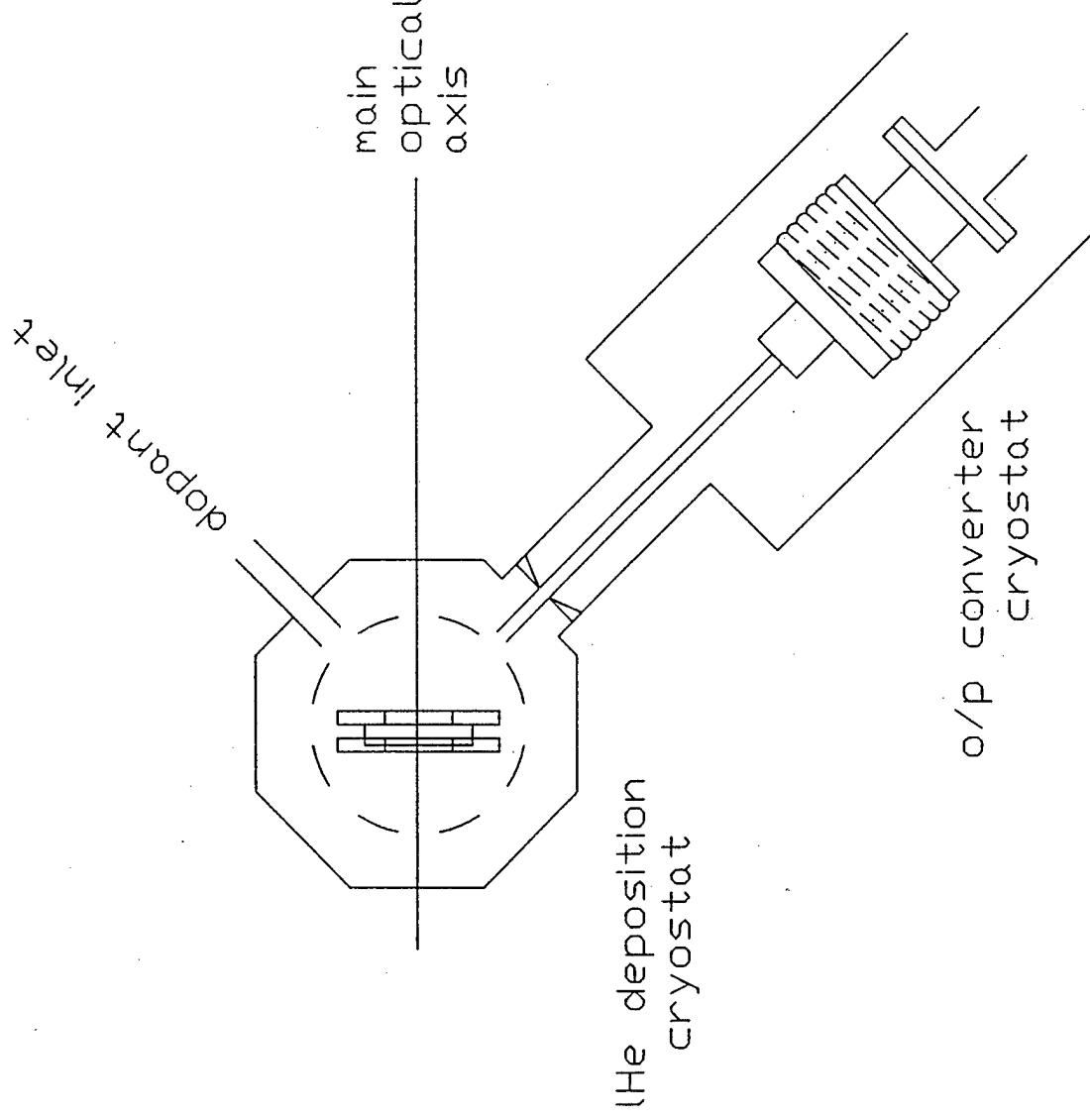
$\underline{(9)}$  — 4



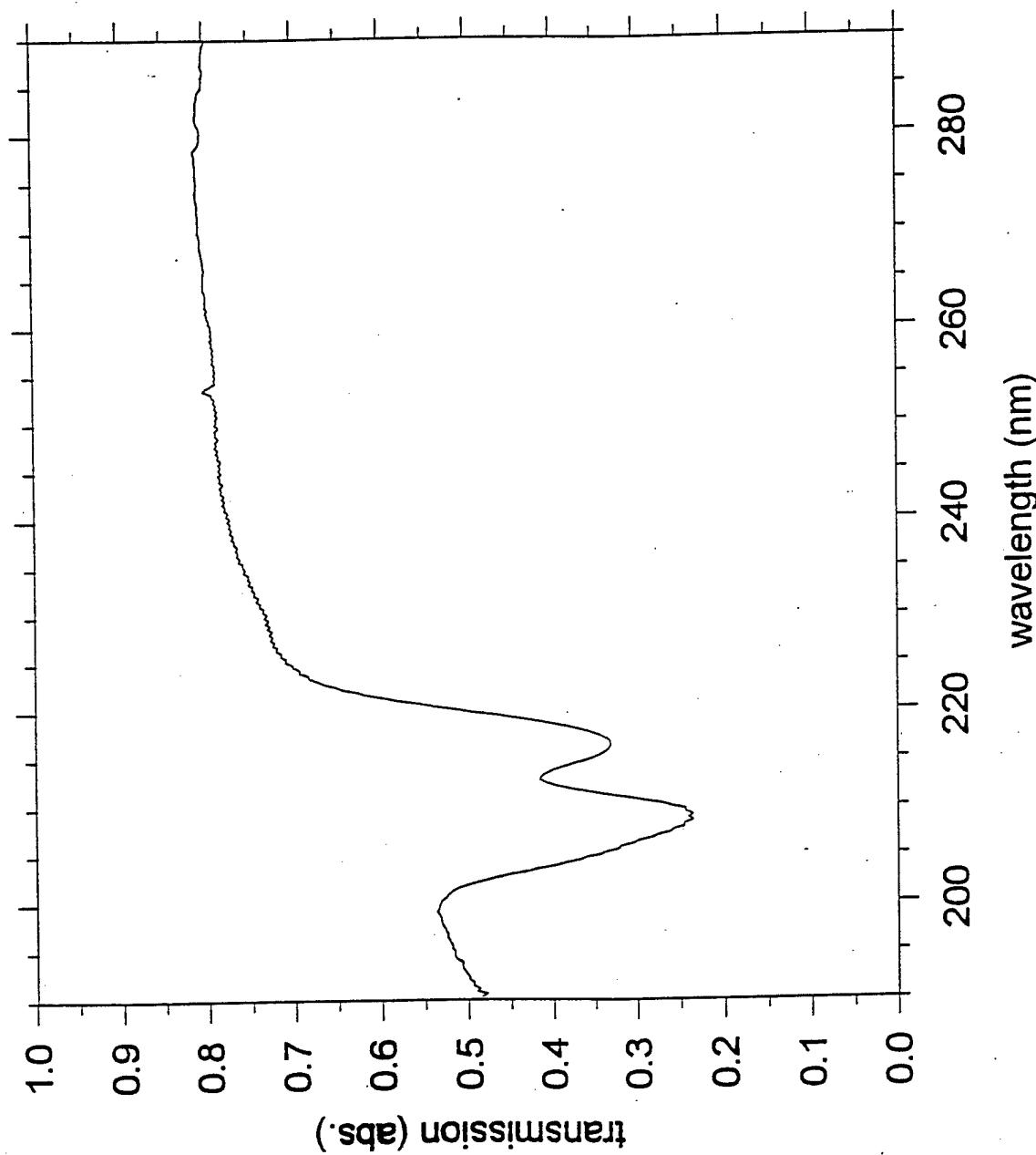
I.F. Silvera,  
Rev. Mod. Phys. 52, 393 (1980).

# Experimental Diagram (c1997)

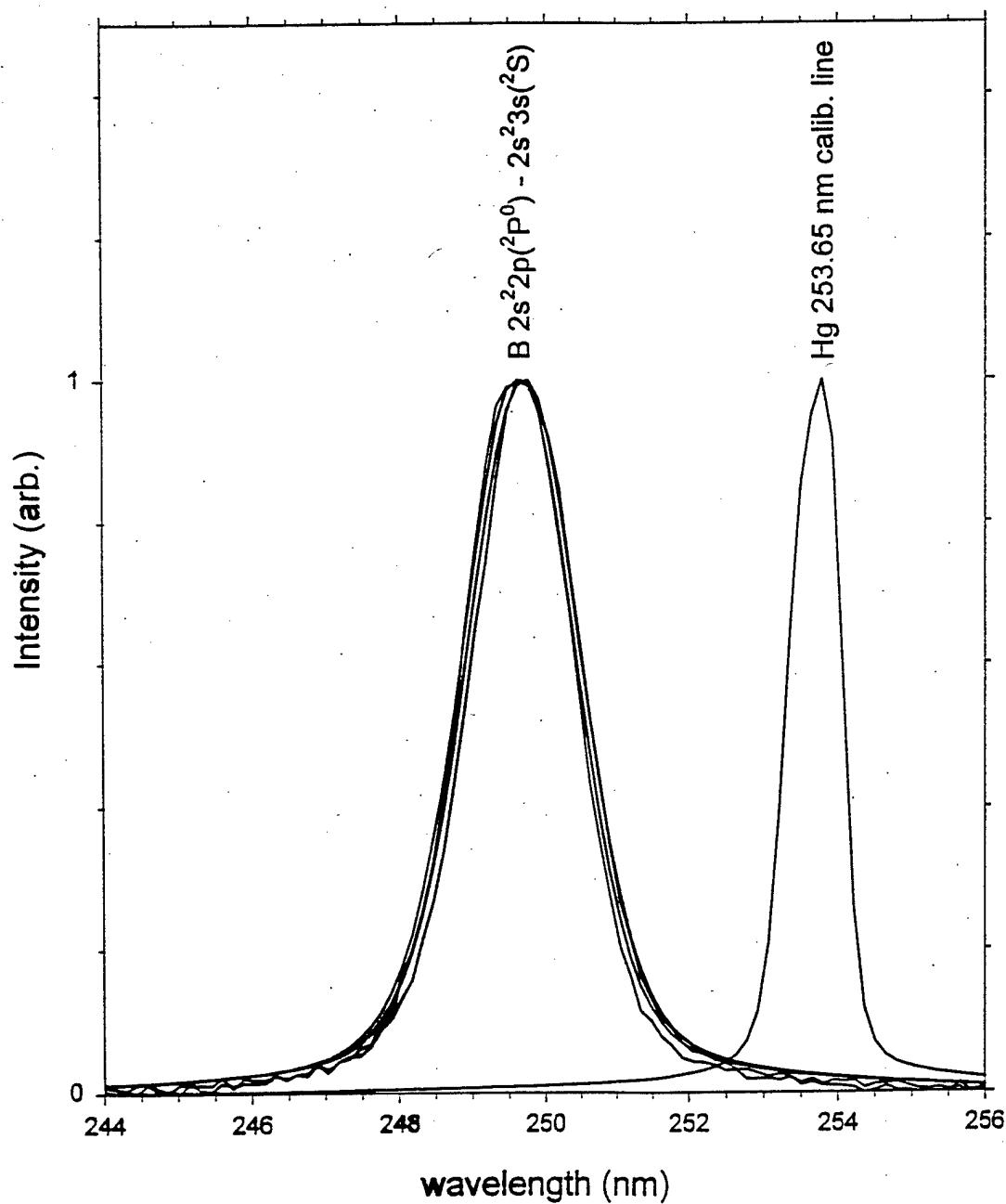
M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998)  
S. Tam and M.E. Fajardo, Rev. Sci. Instrum. **70**, 1926 (1999)



# UV Transmission of 1-mm Thick B/pH<sub>2</sub> Sample



B/pH<sub>2</sub> LIF  
 $\lambda_{\text{exc}} = 207, 210, 217, \text{ and } 220 \text{ nm}$



X

# HEDM Cryosolid Propellants Status

PROOF OF CONCEPT

- \* Demonstrated trapping of several energetic additives in solid hydrogen at concentrations below  $\sim 0.1\%$ .
- \* Demonstrated gram-scale sample production method.

## Outstanding Issues

- \* Increase energetic dopant concentrations above 1 %.
- \* Develop diagnostics for thick, concentrated samples.

# AERL/Edwards Experimental Approach

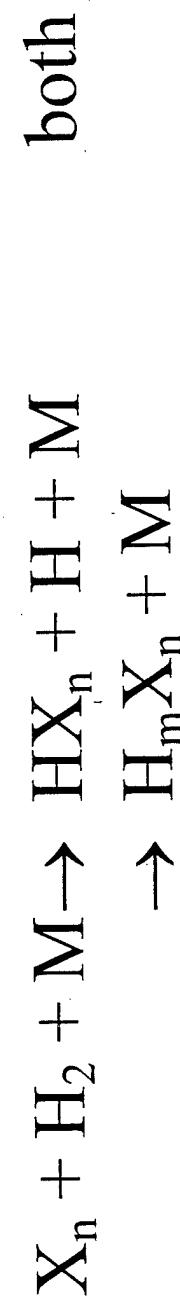
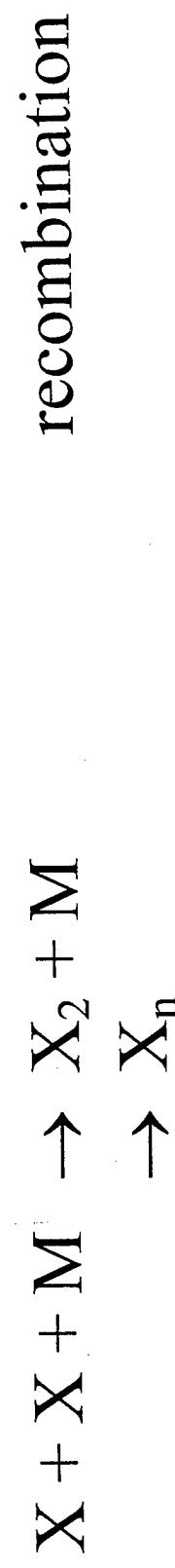
- \* Develop high-flux HEDM dopant sources.  
materials compatibility with liquid B or Al  
Bill Larson's poster
- \* Characterize gas-phase products of HEDM sources.  
MPI/TOFMS  
know species before & after deposition  
Michelle DeRose's poster
- \* Develop IR absorption diagnostics.  
dopant induced IR absorptions  
Simon Tam's poster  
high-resolution IR spectroscopy in solid pH<sub>2</sub>  
My poster and this talk

## HEDM dopant recombination/reaction

- \* ideally:



- \* in practice:



both

# The Perils of Calorimetry

A.M. Bass and H.P. Broida, "Formation and Trapping of Free Radicals" (Academic, New York, 1960).

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GEORGE C. PIMENTEL

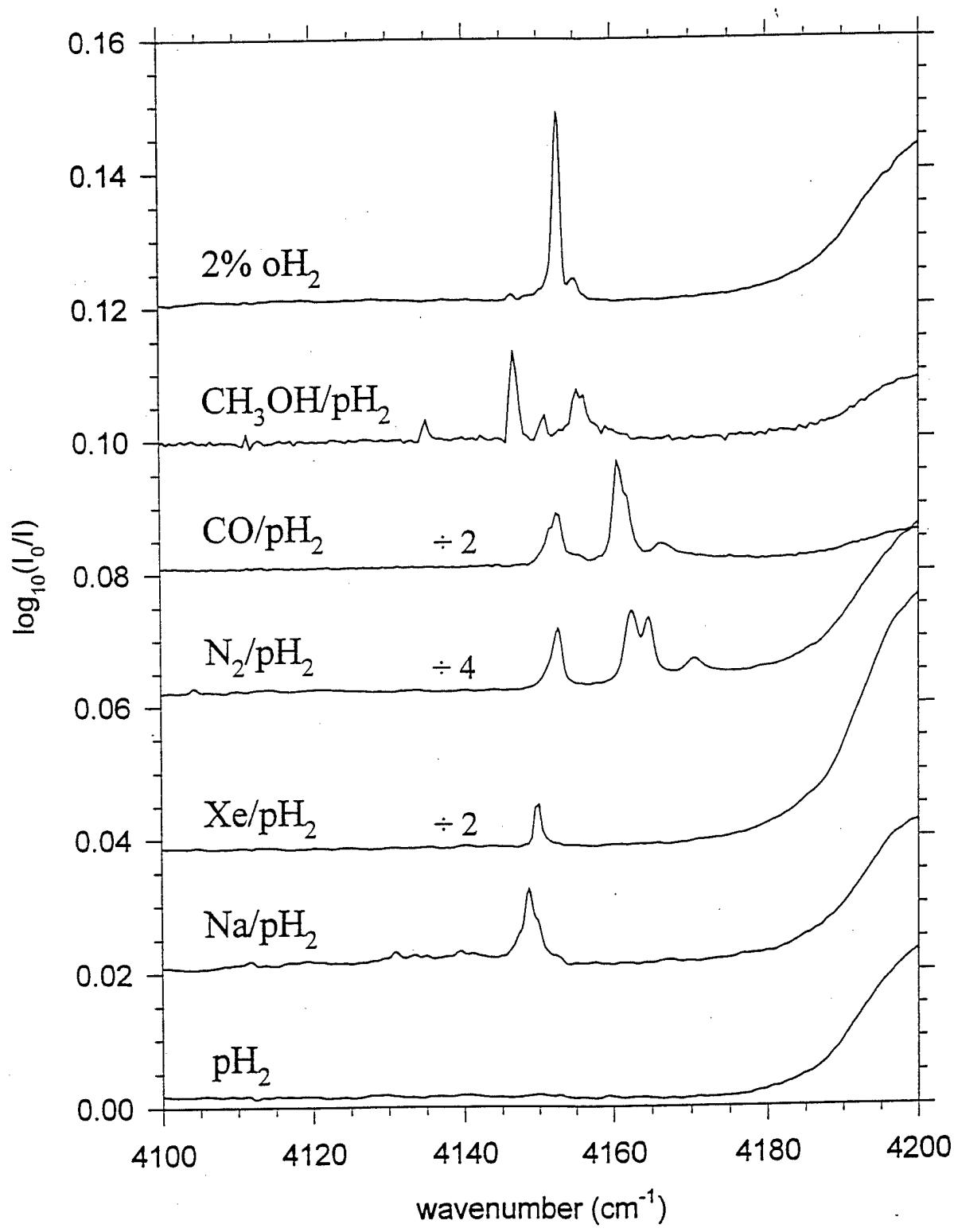
TABLE IX  
CONCENTRATIONS OF FREE RADICALS REPORTED

Radical	Matrix	Mole per cent radicals	Method of production and estimate <sup>a</sup>	Reference
O <sup>•</sup>	O <sub>2</sub>	4-20 <3 ~1	Gas, cal Gas, IR Gas, cal	Minkoff <i>et al.</i> (1959). Harvey and Bass (1958) Broida and Lutes (1956)
OH	Ca(OH) <sub>2</sub>	0.6	$\gamma$ , ESR	R. Livingston <sup>b</sup>
N	N <sub>2</sub>	4 0.2 0.03 >0.03 0.01-0.04	Gas, cal Gas, cal $\gamma$ , ESR Gas, cal Gas, MS	Minkoff <i>et al.</i> (1959) Broida and Lutes (1956) Wall <i>et al.</i> (1959b) Fontana (1958)
	HCOOH	0.2	$\gamma$ , ESR	Fontana <sup>c</sup>
	CH <sub>4</sub>	0.14	$\gamma$ , ESR	Matheson and Smaller (1955)
	CH <sub>4</sub>	0.1	$\gamma$ , ESR	Wall <i>et al.</i> (1959a)
	NH <sub>3</sub>	0.1	Gas, ESR	Wall <i>et al.</i> (1959a)
	HClO <sub>4</sub> -H <sub>2</sub> O	0.1	$\gamma$ , ESR	Cole and Harding (1958)
	H <sub>2</sub> O	0.01	$\gamma$ , ESR	Livingston <i>et al.</i> (1955)
	H, NH <sub>2</sub> (?)	0.01	$\gamma$ , ESR	Matheson and Smaller (1955)
	Alcohols	~0.01	UV, ESR	D. Ingram <sup>b</sup>
	H <sub>2</sub>	0.0006	$\gamma$ , ESR	Wall <i>et al.</i> (1959a)

<sup>a</sup> Abbreviations: gas = rapid condensation of gaseous radicals;  $\gamma$  = gamma ray *in situ* production; UV = photolytic *in situ* production; IR = infrared analysis; cal = calorimetry; MS = magnetic susceptibility.

<sup>b</sup> Private communication.

<sup>c</sup> Fontana, B. J. (1959). *J. Chem. Phys.* **31**, 148.



# High Resolution IR Spectroscopy in Solid $\text{pH}_2$ .

T. Momose, K.E. Kerr, D.P. Weliky, C.M. Gabrys, R.M. Dickson and T. Oka,  
J. Chem. Phys. **100**, 7840 (1994).

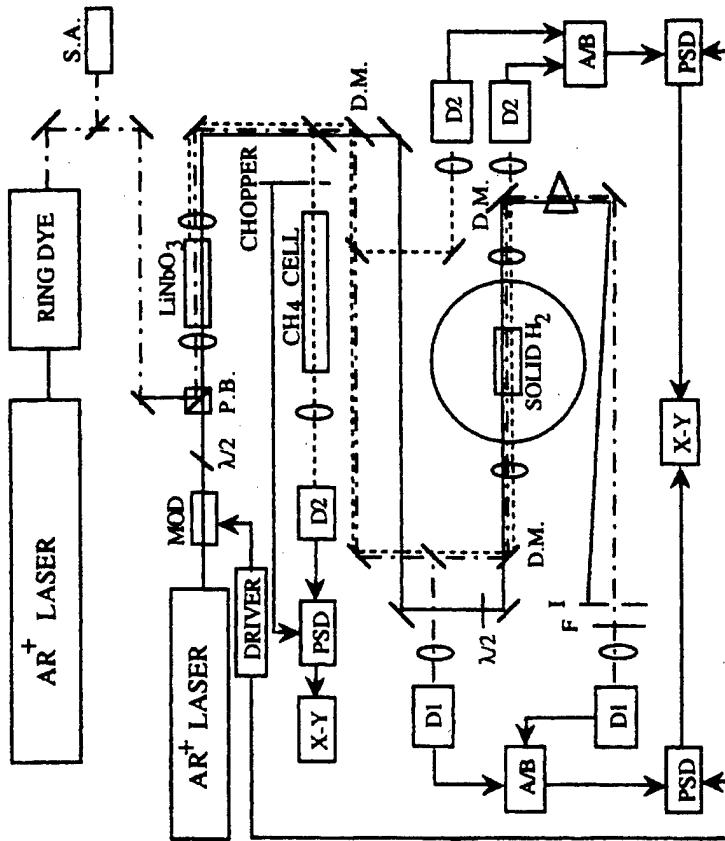
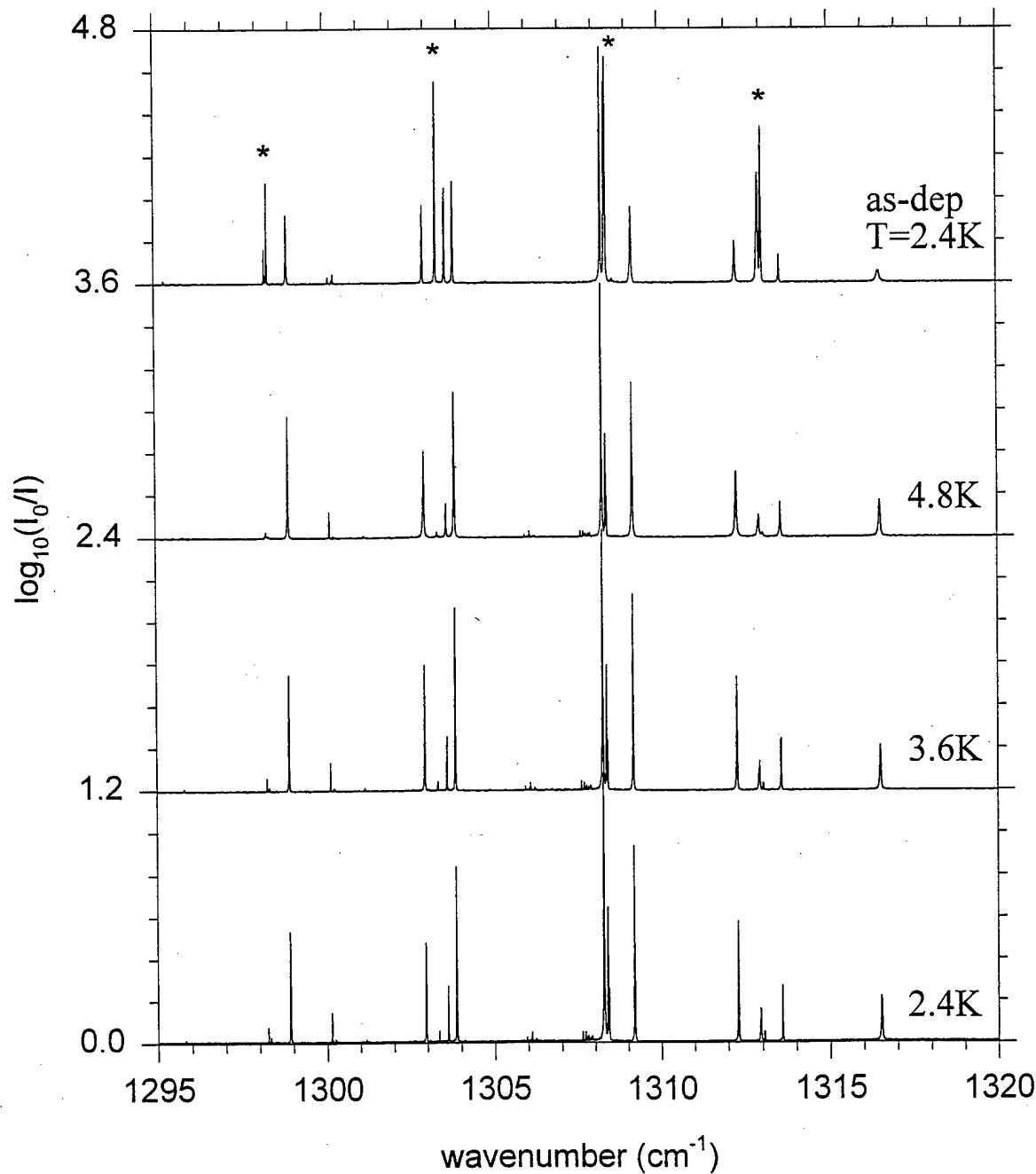
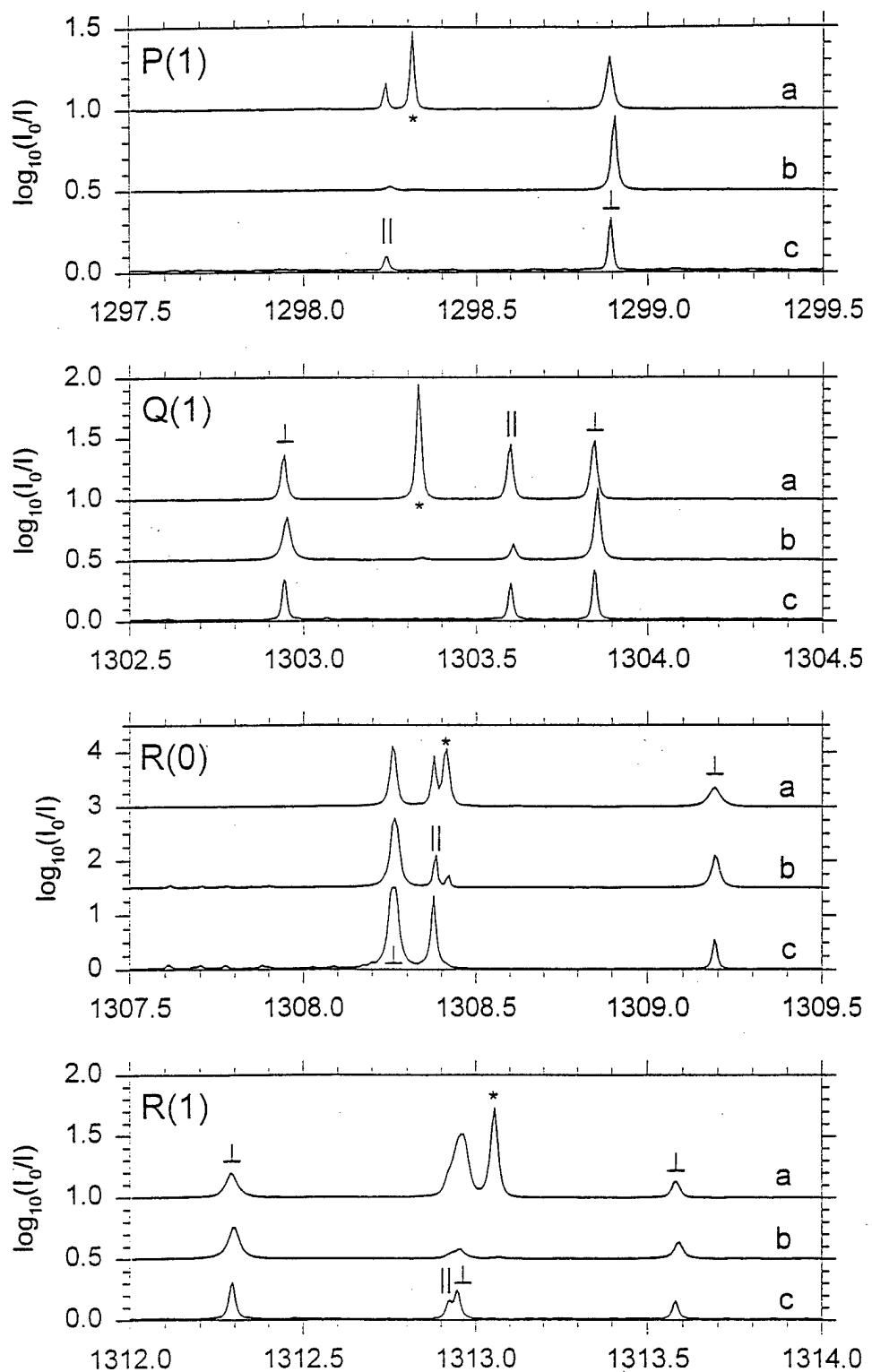


FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of  $\text{LiNbO}_3$  is used for the former and that of solid  $\text{H}_2$  is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.

# $\nu_4$ $\text{CH}_4/\text{pH}_2$ absorptions

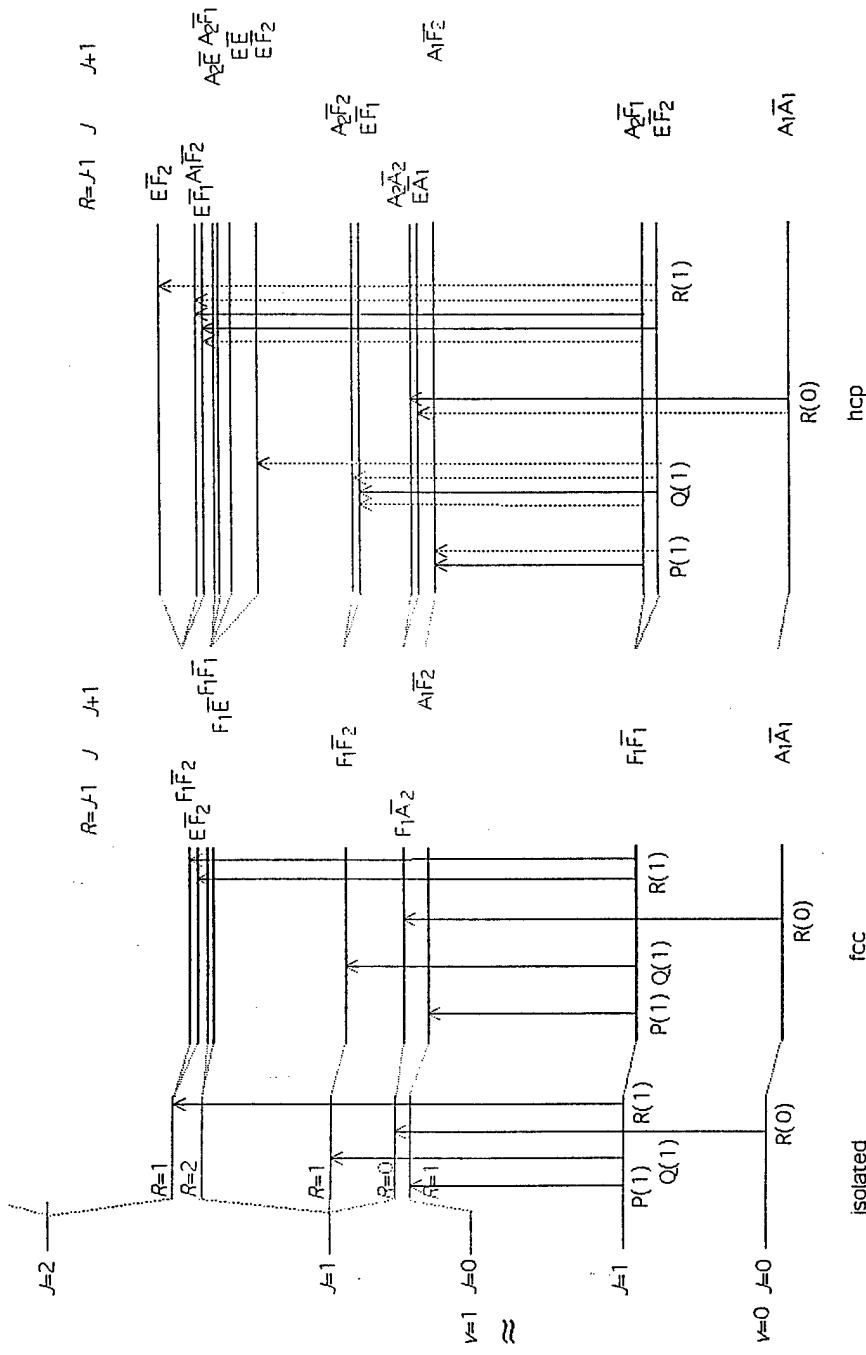


# $\nu_4$ CH<sub>4</sub>/pH<sub>2</sub> Absorptions



## CH<sub>4</sub>/pH<sub>2</sub> Energy Levels

S.S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabashi, and T. Momose, *J. Chem. Phys.*, submitted.



# HEDM Cryosolids Accomplishments

(a list of “things that’ll never work.”)

- \* Trapped Li, B, Na, Mg, Al atoms in solid hydrogen.
- \* Demonstrated production of gram-scale transparent pH<sub>2</sub> solids by rapid vapor deposition.
- \* Demonstrated that vapor deposited pH<sub>2</sub> solids are densest close-packed solids, NOT amorphous.
- \* Generalized phenomenon of dopant induced IR activity in pH<sub>2</sub> host; diagnostic for thick, concentrated samples.

## Future Directions

- \* Develop high-flux HEDM dopant sources.
- \* Characterize gas-phase products of HEDM sources.
- \* Develop IR absorption diagnostics.
  - dopant induced IR absorptions
  - high-resolution IR spectroscopy in solid pH<sub>2</sub>

*[Handwritten signature]*

# National Research Council (1998)

Report: "Maintaining U.S. Leadership in Aeronautics --  
Breakthrough Technologies to Meet Future Air and Space  
Transportation Needs and Goals"

## Assessment:

"Steady progress has been made in research on cryogenic solid propellants. Laboratory experiments have demonstrated the feasibility of ingredient storage, albeit at low concentrations, and small thruster experiments have demonstrated the stable combustion of pure cryo-solid propellants in a hybrid configuration. Much more research will be necessary before this can be called a breakthrough technology and before its readiness for transition into real launch systems can be demonstrated. Research areas are listed below:"

# National Research Council (1998)

Report: "Maintaining U.S. Leadership in Aeronautics --  
Breakthrough Technologies to Meet Future Air and Space  
Transportation Needs and Goals"

## Recommended Future Research Areas:

- \* computational studies of the dynamics, thermodynamics, and spectroscopy of energetic additives to cryogenic solids
- \* Spectroscopic characterization of highly energetic species trapped in energetic matrices at concentrations of at least 1 percent
- \* production methods for energetic species
- \* scale-up production of cryogenic solid propellants with energetic species concentrations of at least 1 percent
- \* methods of transporting and combusting doped cryogenic solids"